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(54) Title: ARTICLES, METHODS FOR CLEANING PRODUCE AND EDIBLE ANIMAL PROTEIN

(57) Abstract

Articles of manufacture, methods, and compositions using toxicologically-acceptable ingredients for cleaning produce and edible animal protein that include foam as an essential element are provided. Articles, methods and compositions are covered whereby a toxicologically acceptable cleaning solution is dispensed to the surface of produce and edible animal protein as a visible foam. The foam provides a positive visual signal as to the extent of cleaning/sanitizing and facilitates increased contact time between the food surface and cleaning solution.

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ARTICLES, METHODS AND COMPOSITIONS FOR CLEANING PRODUCE AND EDIBLE ANIMAL PROTEIN

TECHNICAL FIELD

The present invention relates to compositions, methods for cleaning and/or sanitizing edible animal protein, e.g., meat, seafood and poultry, and produce, e.g., fruits and vegetables, which is intended for ingestion by humans or lower animals, and to articles of manufacture which are especially suitable practicing said methods.

BACKGROUND OF THE INVENTION

It is well-known and appreciated by consumers that fruits, vegetables and edible animal protein sources such as meat, seafood and poultry should be thoroughly washed prior to ingestion in order to remove soils and other unwanted residues which may be undesirably clinging to the surfaces thereof. In addition, some consumers wish to remove the artificial "waxy" coatings which may be applied to some fruits to retard moisture loss for increased storage life and to enhance their appearance. It has been estimated that 95% of consumers recognize the need for thorough washing but, ordinarily, only use tap water for this purpose. On the order of 5% of those consumers who do wash their vegetables use a household cleaner. typically a liquid dishwashing product, to help ensure cleanliness. However, dishwashing products are not specifically intended for such use, inasmuch as they are usually designed to provide high, persistent suds which makes them inconvenient to remove from the fruits or vegetables which have been washed therewith. It will also be appreciated that the formulation of truly effective compositions, especially those which can be used safely by individual consumers, for washing edible animal protein and produce presents a unique problem to the formulator, inasmuch as many artdisclosed cleaning ingredients would, presumably, not be desirable for use in direct contact with foods where they might not be fully removed.

Moreover, it would be especially desirable to provide methods and articles of manufacture that comprise effective, toxicologically-acceptable cleaning compositions for produce and edible animal protein in the form of solutions which are clear or which have only minimal haziness and that easily rinse from the food surface. Liquid solutions are convenient for the user, since they can be applied

directly to soiled produce, and edible animal protein followed by rinsing in tap water. The clarity of the liquids connotes cleanliness to the user and is thus highly desirable. However, the use of clear cleaning solutions on food pose problems of determining proper or adequate coverage over the food surface. The very same properties that connote cleanliness, i.e. clear liquids, do not provide positive visual signals of where the cleaning solution has been applied and where it has not. Furthermore, the nature of cleaning solutions, typically low viscosity mobile solutions, result in rapid run-off of the solution making it difficult to ensure extended contact times often required for thorough cleaning.

It has now been discovered that methods that employ a foam of cleaning solution address the needs noted above. It has been discovered that preferred methods using a foam and articles dispensing can use cleaning solutions in the basic pH range and yet possess a desirable clean feel to the users' hands.

BACKGROUND ART

The use and selection of cleaning ingredients for the purpose of washing fruits and vegetables is described by the United States Code of Federal Regulations, Title 21, Section 173.315: "Ingredients for use in washing or lye peeling of fruits and vegetables". These regulations restrict the ingredients that may be used for direct contact with food to those described as "generally regarded as safe" (GRAS), and a few other selected ingredients. These sections also provide certain limitations on the amount of material that can be used in a given context.

Among these ingredients, the experienced formulator will find only a few ingredients which can provide effective cleaning of hydrophobic residues, such as waxes, oils, or man-made chemical residues such as pesticides. It is recognized these types of residues are removed most readily by surface active ingredients in water, or by organic solvents largely in the absence of water. Other types of soils, especially particulate insoluble soils that do not readily disperse in water, are effectively removed by surface active materials in water, especially when aided by complex anionic salts, such as citrates (polycarboxylates), or polyphosphate salts.

Within this limited group of ingredients the range of effective cleaning compositions well suited to the task of cleaning fruits and vegetables, especially as practiced by individual consumers, have not been previously described. It is desirable to formulate liquid compositions which are amenable to direct application to edible animal protein and produce, preferably by spray application. Further, it is desirable the compositions are easily rinsed, without leaving residue. Preferred compositions should be mild to the hands, especially for direct application.

Food Chemical News, Inc., 1991, p. 334.1, reports that PEG 200-9500 has been cleared under §178.3750 as a component in articles for use in contact with food (Fed. Register, Oct. 15, 1968). Nonetheless, for washing produce, polyethylene glycol should be affirmed as GRAS.

A thorough review of polysaccharides and their derivatives can be found in Whistler, R. L., <u>Industrial Gums</u>, Academic Press (New York, 1959).

Compositions useful in the methods and articles described herein can be found in U.S. Patent Nos. 5,498,295; 5,500,048; 5,500,143; 5,503,764; and 5,549,758 which are incorporated herein by reference.

SUMMARY OF THE INVENTION

The present invention encompasses compositions, methods and articles for cleaning and/or sanitizing edible animal protein, e.g., meat, seafood and poultry, and produce, e.g., fruits and vegetables, which is intended for ingestion by humans or lower animals. The present invention comprises several aspects including:

- I. An article of manufacture comprising a spray container, suitable for use by an individual to clean produce and edible animal protein, containing a toxicologically acceptable cleaning solution, said cleaning solution being capable of being dispensed with a clearly visible content of foam from said container;
- II. A method for cleaning produce and edible animal protein whereby a toxicologically acceptable cleaning solution is dispensed to the surface of said produce and edible animal protein as a visible foam; and
- III. Toxicologically acceptable cleaning solution compositions comprising ingredients useful for cleaning/sanitizing produce and edible animal protein, wherein said compositions further comprise a foam enhancing component, said composition capable of being dispensed as a visible foam.

The essential foam element of the present invention serves several useful purposes. It provides a positive visual signal to the consumer that the cleaning solution is present. The foam also acts to prevent the cleaning solution from immediately running off the food surface. The ability of the foam to retain the cleaning solution to the food surface is particularly important when the residence time of the cleaning solution on the food surface is critical to the cleaning and/or sanitizing function of the solution. Preferably the article is capable of dispensing a foam that remains visible for at least 3 seconds, more preferably at least 1 minute.

The desired foam effect can be achieved by either mechanical means, i.e. foaming spray head, or by careful formulation, i.e. addition of components to the cleaning solution which facilitate foaming when dispensed. The selection of ingredients useful to cause foaming when dispensed is critical. Traditional foaming

means such as detergent surfactants do not perform well in the context of methods used to clean food surfaces due to the difficulty in rinsing persistent sudsing detergents, and in formulating such detergents into compositions which would be acceptable if ingested.

Preferably, the careful formulation of cleaning solutions that facilitate foaming when dispensed comprise non-detergent foam enhancing components. The term "foam enhancing component" is defined as an ingredient added to the formulation which increases either the volume of foam that can be generated from a given amount of solution or increases the time the foam persists once dispensed to the food surface. Preferably the non-detergent foam enhancing components are selected from polymeric shear-thinning thickeners; more preferably selected from the substituted celluloses, modified polysaccharides, and naturally occurring gums; and even more preferably xanthan gum.

Specifically the invention includes a method for cleaning produce comprising contacting the surfaces of said produce by direct application of a toxicologically acceptable cleaning solution as a visible foam, preferably a foam that remains visible for at least 3 seconds, more preferably at least 1 minute, typically comprising:

- (a) from about 0.01% to about 15% of C₈-C₁₈ fatty acid;
- (b) optionally, from about 0.1% to about 4% by weight of nonionic surfactant, especially ethoxylated/propoxylated adducts of aliphatic C_{12-18} alcohols;
- (c) optionally, from about 0.1% to about 4% by weight of organic polycarboxylic acid, preferably citric acid;
- (d) optionally, up to about 0.2% by weight of an acid-stable anionic surfactant such as the alkali or alkaline earth salts of dodecylbenzene sulfonate;
- (e) optionally, a toxicologically-acceptable basic buffer such as potassium and/or sodium salts of carbonate and/or bicarbonate;
- (f) optionally, a toxicologically-acceptable preservative;
- (g) optionally, at least about 0.05%, by weight, of water-soluble polyethylene glycol having a molecular weight of about 200, or higher;
- (h) optionally, a toxicologically-acceptable acidic buffer, other than said polycarboxylic acid and/or said fatty acid, sufficient to maintain the desired pH, preferably from about 0.05% to about 10% of phosphoric acid;
- (i) the balance comprising an aqueous carrier selected from water and, optionally, low molecular weight, toxicologically-acceptable organic solvent such as ethanol, glycerol, etc.;

wherein said aqueous solution has a pH in the range of 8 or greater, preferably from about 9.5 to about 12.5, and preferably employs potassium carbonate as buffer (e) to provide a pH of about 11, said composition preferably being essentially free of any material that is not toxicologically acceptable. The invention also includes articles comprising a spray container, suitable for use by an individual to clean produce and edible animal protein capable of dispensing this cleaning solution as a clearly visible foam.

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The present invention also encompasses compositions comprising components (a) though (i) noted above which further comprise a foam enhancing component, preferably a polymeric shear-thinning thickener, more preferably selected from the substituted celluloses, modified polysaccharides, and naturally occurring gums; and even more preferably xanthan gum; said composition being capable of being dispensed as a visible foam, preferably a foam that remains visible for at least 3 seconds, more preferably at least 1 minute.

The inventions herein can also encompass a more specific method for cleaning produce and edible animal protein at a basic pH of from about 8.0 to about 12.5, preferably more than about 9.5, comprising contacting the surfaces of said produce and/or edible animal protein with a foam of a toxicologically acceptable cleaning solution, preferably an aqueous cleaning solution comprising potassium oleate, preferably at a level of more than about 0.5%. Potassium oleate is mild, rinses well, has minimal odor, is effective in removing unwanted materials, especially wax, from apples, does not oversuds, and is very safe, even when the composition is misused and the produce, or edible animal protein, etc., is not completely rinsed. Therefore, it is a uniquely preferred surfactant for use in cleaning food materials. The potassium cation is much more useful than the sodium cation since the potassium oleate is quite soluble whereas the sodium oleate tends to form a less soluble soap, especially at low temperatures.

Another preferred, concentrated, alkaline method for cleaning produce and edible animal protein comprises contacting the surfaces of produce or edible animal protein with a foam of a cleaning solution containing from about 0.5% to about 15%, preferably from about 0.75% to about 8%, more preferably from about 1% to about 5%, detergent surfactant, preferably one that is GRAS, and more preferably said cleaned surfactant said cleaning solution having a pH of from about 8 to about 12.5, preferably from about 9.5 to about 12.3, especially when the detergent surfactant is a soap such as the said cleane, more preferably from about 11 to about 12. Such compositions when used in an effective amount to clean apples coated with wax, will provide effective removal of the wax. Removal of wax from apples is one of the

most difficult cleaning tasks and therefore is indicative of overall superior performance.

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Yet another preferred variation in the above methods for cleaning produce and edible animal protein involves placing said cleaning solutions in a spray container capable of providing a foam of said solution to distribute the said solution, or solutions, over the surfaces of the produce while utilizing only a minimum amount of the cleaning solution and minimizing the exposure of the remaining solution to the atmosphere, where the solution is more likely to be contaminated and/or exposed to oxygen, both of which tend to cause undesirable changes in the solutions from aesthetic and/or performance considerations. In such spray processes, there is only need for a relatively small amount of material in the package, and for individual consumer use, this is desirable, since some consumers will not be able to manipulate large weights. For consumer usage, typically, the container will contain no more than about two gallons (about four liters), especially when the container is a spray container, even one that has a tube that permits the spray device to be manipulated while the bulk container remains in place. Preferably such spray containers contain about one liter, or less, of cleaning solution.

Preferred compositions used in the methods and articles described herein contain only materials that are GRAS to protect against possible misuse by the consumer. Traditionally, most suggestions for cleaning of fruits and/or vegetables have contemplated a commercial scale where there is typically more control over the conditions, especially the amount and thoroughness of rinsing. The present invention, especially the methods involving use of hand held trigger activated spray means are primarily/solely suitable for use by individual consumers so that it is essential that extra safety be built into the product. Failure to rinse thoroughly after cleaning is less of a concern if all of the ingredients are GRAS. This is especially important when concentrated basic compositions suitable for removal of wax from apples are used. The larger amounts of materials needed for removal of wax create an heretofore unknown level of risk for the individual consumers, many of whom are not likely to read, or follow, instructions which would permit safe use of non-GRAS materials.

The ingredients in the above compositions are preferably selected and used in proportions which provide substantially clear compositions. Substantially clear includes only minimal haziness, and preferably the compositions are completely clear. The ingredients are also selected to have minimal odor, both initially and after storage. The lack of odor is especially important in compositions for use on food. The compositions preferably have a viscosity that is more than about 10 centipoise,

preferably more than about 50 centipoise when at rest, but thin under shear to permit easy dispensing, especially from spray containers.

Below pH about 9.7, the compositions can exhibit some objectionable fatty acid odor. Even at the optimal pH's above 11, some odor can persist. In order to mask this odor, the compositions can contain a perfume or essence ingredient. Especially preferred for this use are terpenes derived from citrus fruit, e.g., oranges, lemons, limes, grapefruits, tangerines, tangelos, etc.

All documents cited are incorporated herein by reference.

DETAILED DESCRIPTION OF THE INVENTION

The following components and toxicologically-acceptable ingredients are used in the preparation of the compositions used in the preferred methods and articles described herein. By "toxicologically-acceptable" is meant that any residues from the ingredients of the compositions which may remain on the fruits or vegetables cleansed therewith are safe for ingestion by humans and lower animals. By "edible animal protein" is meant to include foodstuffs which are comprised essentially of the protein found in such foods sources including, but not limited to, beef, pork, chicken, turkey, fish, shellfish and game meats such as venison, rabbit and the like. Said edible animal protein includes the processed forms of said protein sources, including, but not limited to, such forms as ground beef, ground turkey, bologna, hot dogs, sausages, fish cakes, and the like.

Spray Container - The compositions herein are preferably used by placing them in a package comprising either an aerosol container or a non-aerosol spray device "spray means." Said spray means is any of the manually activated, preferably "trigger-type," means for producing a spray of liquid droplets as is known in the art. Typical spray means are disclosed in U.S. Pat. Nos.: 4,082,223, Nozawa, issued Apr. 4, 1978; 4,161,288, McKinney, issued July 17, 1979; 4558,821, Tada et al., issued Dec. 17, 1985; 4,434,917, Saito et al., issued Mar. 6, 1984; and 4,819,835, Tasaki, issued Apr. 11, 1989, all of said patents being incorporated herein by reference. The spray bottle, or container can be any of the ones commonly used for containing hard surface cleaner detergent compositions. Examples of bottles are those in U.S. Design Pat. Nos.: 244,991, Weekman et al., issued July 12, 1977; and 275,078, Wassergord et al., issued Aug. 14, 1984, said patents being incorporated herein by reference.

The spray means herein can also include those that incorporate a propellant gas into the liquid and those that will foam even compositions having a viscosity of less than about 15 cps. The spray means herein are typically those that act upon a discrete amount of the composition itself, typically by means of a piston that

displaces the composition and expels the composition through a nozzle to create a foam of thin liquid. The spray means can include a foaming spray head such as those described in U.S. Pat. Nos.: 4,350,298; 4,730,775; 4,883,227; and 4,890,792 all of said patents being incorporated herein by reference. An example of an acceptable commercially available foaming spray head is model TS-800 with foaming nozzle manufactured by Calmar, Inc..

Polymeric Shear-thinning Thickener - The polymeric shear-thinning thickener can be any of the shear-thinning thickeners known in the art to thicken liquid compositions and especially aqueous compositions. Substituted cellulose materials, e.g., carboxymethylcellulose, hydroxymethylcellulose, etc., and naturally occurring thickeners like carrageenan and xanthan gum are useful herein. Xanthan gum is the preferred thickener. Xanthan gum is disclosed in U.S. Pat. No. 4,788,006, Bolich, issued Nov. 29, 1986, at Col. 5, line 55 through Col. 6, line 2, said patent being incorporated herein by reference.

The preferred toxicologically acceptable cleaning compositions described hereinbefore can be thickened by a process in which the thickener is added, preferably in fully hydrated form, at a level of from about 0.001% to about 1%, preferably from about 0.005% to about 0.5%, more preferably from about 0.01% to about 0.3%, to raise the viscosity of a composition whose viscosity is less than about 15 cps to from about 15 to about 250, preferably from about 15 to about 100 cps. If the viscosity is too low, the foam is not visible and at even the slightly higher viscosities, the area covered by the foam spray pattern starts to decrease substantially and the foam becomes more difficult to rinse easily from the food surface.

The viscosity is determined using a Brookfield Synchroelectric Viscometer, model LVT, made by Brookfield Engineering Laboratory, Inc., Stoughton, Massachusetts, using a No. 1 spindle at 60 rpm, and at a temperature of about 20oC. (Constant shear rate of about 13 inversed seconds.)

Shear-thinning characteristics of, e.g., polymers and/or compositions, are determined using a Carrimed Controlled Stress Rheometer Model CSL 100, made by Carrimed Ltd., Interpret House, Curtis Road Estate, Dorking, Surry RH 4 1DP, England. The Rheometer employs double concentric cylinders geometry to make steady shear measurements at various shear rates. These measurements are made at about 26oC. The shear-thinning, pseudoplastic behavior of the xanthan gum system can be mathematically modeled by the equation:

$$N = KR^{n-1}$$

where N is the apparent viscosity, K is the consistency constant, R is the shear rate, and n is the shear index. For best spraying results (dispensing) the values of K and n

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should give viscosities below 15 cps at spraying shear rates (~10,000 inversed seconds, as reported in trade literature).

Shear-thinning behavior is described in U.S. Pat. No. 4,783,283, Stoddart, issued Nov. 8, 1988, especially the portion appearing at column 2, line 46, et seq.

Nonionic Surfactant - The nonionic surfactant is preferably selected from materials known well-known in the art, such as alkylene oxide (ethylene oxide or propylene oxide) adducts of C₁₀₋₁₈ aliphatic alcohols or acids, C₁₀₋₁₈ aliphatic alcohol adducts of glucose (alkyl polyglucosides). The specific nonionic surfactant selected ideally has a hydrophilic-lipophilic balance (HLB) greater than about 10, and a cloud point above about 35°C in the composition. The United States Code of Federal Regulations (CFR) specifically describes an ethylene oxide/propylene oxide adduct of C12-18 aliphatic alcohol of molecular weight of about 800. Such a material is available as PLURAFAC RA-20 (BASF).

It is to be appreciated that in the acidic compositions herein, the alkoxylated alcohol functions substantially as a cleansing agent, whereas in the basic compositions the alkoxylated alcohol functions mainly as a dispersant for any soap curd which may form during the cleansing operation. Further, it is recognized that the selection of non-nitrogen containing nonionics can minimize the possibility of microbial growth in the dilute surfactant compositions.

Fatty Acid and/or Salts Thereof - The acidic compositions herein are formulated using an unsaturated fatty acid; oleic acid is preferred and convenient for this use. However, the particular oleic acid that is selected should preferably be low in polyunsaturates, e.g., contain less than about 10%, preferably less than about 7%, more preferably less than about 5% and will typically have an Iodine Value (IV) of from about 70 to about 100, preferably from about 83 to about 95, more preferably from about 85 to about 90. Polyunsaturated fatty acids are not preferred herein, due to odor problems. However, this is primarily from aesthetic considerations since such acids are effective in cleaning. The amount of polyunsaturated fatty acids should be less than about 8%, preferably 0%. The amount of polyunsaturated fatty acids with more than about two double bonds should be less than about 1%, preferably 0%. Saturated fatty acids are unacceptable as they have limited solubility for longer chainlength materials ($\ge C_{12}$), or have unacceptable odor ($\le C_{14}$). For example, stearic and/or tallow fatty acids soaps, even potassium soaps, do not have enough solubility at room temperature, where most produce cleaning is done by individual consumers, to formulate even compositions containing the minimum of about 0.1% soap required for acceptable cleaning. Other specific solubilizing surfactants in higher proportions would be required to solubilize these saturated fatty

acids. Pamolyn 100 FGK oleic acid is a good example of a suitable commercial fatty acid.

Polyethylene Glycol - The water-soluble polyethylene glycol polymer (PEG) employed herein is the known article of commerce and is available under a variety of trade names, of which CARBOWAX (Union Carbide Corporation) is exemplary. PEG's in the average molecular weight range of from about 200 to about 20,000 can be used herein, and PEG as CARBOWAX in the average molecular weight range of at least about 400, typically 400 to about 9500, is convenient and preferred. As disclosed above, the compositions herein will comprise at least about 0.05%, by weight, of the PEG and will typically comprise from about 0.1% to about 10%, by weight, of PEG. The amounts used can vary with the molecular weight of the PEG, the amount of oleate or other fatty acid used in the composition, the desired viscosity of the composition, and like factors within the discretion of the formulator. The following Table 1 illustrates the variation in viscosity which can be effected using various levels of PEG and varying PEG molecular weights in a liquid composition (Control) comprising 3% potassium oleate. Table 1 also illustrates the effect of sodium benzoate (Bz) on viscosity.

Table 1
Viscosity (cP* as made)Viscosity (cP* as made)

Composition	72°F (22°C)	43°F (6°C)
Control (no PEG)	7	110
Control + 0.674% Bz	23	1000
Control + 0.118% Bz	7 .	159
Control + 0.1% PEG 400	5	36
Control + 0.5% PEG 400	2	17
Control + 0.1% PEG 8000	5	23
Control + 0.5% PEG 8000	8	4

^{*}Viscosity in centipoise as measured using Brookfield LVTD #2 spindle, 60 rpm at the designated temperature.

In a typical mode, the preferred compositions herein that have an improved tactile impression will comprise oleate:PEG weight ratios in the range from about 1:2 to about 15:1, preferably from about 1:1 to about 10:1.

<u>Tactile Impression</u> - The compositions herein which contain the polyethylene glycol are characterized not only by their excellent cleaning performance and sudsing/rinsability properties, but also by their improved viscosity properties and improved "feel". While, as disclosed above, the improved viscosities of the compositions herein are readily demonstrated quantitatively using standard

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measurement techniques, the improved feel of the compositions which come into contact with the users' hands is a qualitative tactile impression. However, this improved, "non-slippery", "non-soapy" improvement in skin feel can be demonstrated by rubbing Test (PEG-containing) and Control (no PEG) compositions on the hands or inner forearms of volunteer graders. Even in such rudimentary tests, the graders can readily distinguish the improved tactile impression of the compositions made in accordance with this invention.

Optional Surfactants - Optionally, acid or base stable anionic surfactants can be employed, as allowed by the United States Code of Federal Regulations, Title 21, Section 173.315. Preferred are salts of dodecylbenzene sulfonate, typically at levels up to 0.2%. Also described in the CFR are phosphate esters of ethylene and/or ethylene/propylene oxide adducts of aliphatic alcohols, dioctyl sulfosuccinate, or 2-ethylhexyl sulfate, typically but these materials suffer from lack of stability at either acid or basic conditions.

Sequestrant/builder - The organic polycarboxylic acid, or salt thereof, e.g., citric acid, is used as a sequestrant/builder in the acidic compositions herein or sodium and/or potassium citrate as used in the basic compositions herein are standard items of commerce. Other organic poly carboxylic acids, especially those that are GRAS, such as tartaric, malic, etc. acids, can also be used. When formulating the basic formulations herein, it is preferred to use the potassium salt, as compared with the sodium salt, to provide ease of formulatability. Complex phosphates can also be used, but are generally avoided due to regulatory considerations.

Buffer - Toxicologically-acceptable acidic or basic buffers can be used in the compositions herein to maintain product pH in the acid or base range. For ease of formulatability, it is highly preferred that such acidic and basic buffers be in their potassium salt form. Citric acid is a preferred acid pH buffer, and in the basic pH systems, potassium citrate is a preferred dispersant for particulate soils. Potassium carbonate is a convenient and preferred basic pH buffer. Sodium bicarbonate is a highly desirable material to add to the compositions of this invention as a part of the buffering system since it is readily available as baking soda in food grade and is therefore relatively inexpensive, while providing a highly desirable purity to the composition. Compositions formulated with a mixture of potassium and sodium cations in molar ratios of from about 1:1 to about 10:1, preferably from about 2:1 to about 8:1, more preferably from about 4:1 to about 5:1 potassium to sodium, e.g., as provided by mixtures of potassium hydroxide (hydrate) and sodium bicarbonate, have desirable rheological properties. The compositions are thick, so as to cling to the fruit or vegetable until spread, but are readily dispensed, e.g., by means of a spray

device, either aerosol or finger-activated pump. The levels and identities of the ingredients are adjusted to provide products having the desired viscosities as set forth herein, e.g., more than about 5, preferably more than about 10, more preferably more than about 50 centipoise when at rest, and less than about 150, preferably less than about 100, more preferably less than about 100, more preferably less than about 50 centipoise under shear of $\geq \sim 1000$ sec-1.

The ability of the preferred compositions containing mixtures of both sodium and potassium cations to shear thin is important to promote easy dispensing, especially when the compositions are sprayed, while maintaining the ability to be thick, cling, and delay run off after being applied to the produce.

The pH is preferably not greater than about 12.5, and especially does not contain large amounts of buffer at higher pHs for consumer safety, especially when the compositions are sprayed.

<u>Preservative</u> - Standard food-grade preservatives such as potassium sorbate/sorbic acid and/or sodium benzoate/benzoic acid, or mixtures thereof, are suitable for such purposes. For example, from about 0.01% to about 0.2% of benzoic acid or its sodium or potassium salts can be used. In general, the basic pH compositions herein do not require a preservative, although one can be added if desired.

Antioxidants The use of commercial oleic acid, or oleate salts, can be complicated by development of off-odors and/or yellowing of the compositions in which they appear. These undesirable properties are believed to be caused by complex side reactions initiated by the reaction of oxygen with primarily the polyunsaturated components of the fatty acid stock. These results can be avoided, or minimized, by avoiding contact with air, or by controlling the quality of the fatty acid stock so that the amount and type of polyunsaturates are minimized as described above, and/or by the addition of antioxidants.

It has been found, that the addition of tocopherols (e.g., Vitamin E, or tocopherol acetates) in alkaline formulations is advantageous, as they do not degrade, nor do they impart a strong color. They inhibit the development of off-odors for extended periods of time so that the need for masking scents is minimized, or eliminated, particularly for oleic acid stocks of high quality, as described above. The use of butylated phenols, such as BHT and BHA is also useful, but their effectiveness appears more limited and they can impart stronger colors to the compositions. Other food grade antioxidants such as Vitamin C and sulfites, are desirable to prevent deterioration of the compositions by the action of oxygen, but care must be taken

since vitamin C can suffer color degradation and sulfites can cause odor problems. Sulfites also have been the target of potential health concerns.

Fluid Carrier - The major proportion (typically, 90%-98%, by weight) of the compositions herein comprises water as the solubilizing carrier for the ingredients. As noted in the Examples hereinafter, water-ethanol can also be employed and is especially preferred when formulating basic pH compositions herein. The ethanol level preferably should not exceed 2% in the solution used to clean the produce, to avoid an alcoholic odor, especially when spraying. Other compatible, water-soluble, low molecular weight solvents such as glycerol can also be used.

Preferred articles include the compositions herein that are suitable for use in the processes described herein, in a package that can provide a foam. Such articles are not widely marketed. This is surprising in view of the clear advantages for such products for use by individual consumers. The typical use involves treating individual items of produce or edible animal protein, which would make preparation of a "bath" wasteful.

In a preferred process for using the products described herein, and especially those formulated to be used at full strength, the product is sprayed onto the food product to be cleaned, rubbed, rinsed and/or wiped off with a suitable material like cloth, sponge, a paper towel, etc. The compositions and processes described herein, especially those that are alkaline, can provide effective disinfectancy.

The compositions and processes described herein can also provide effective disinfectancy/sanitization. In order to provide good kill of microorganisms, especially bacteria, one should use high concentrations and/or longer exposure times. Typically, the products should be used full strength and allowed to remain on the edible animal protein or produce for at least about one minute, preferably at least about five minutes, and, for some microorganisms, even ten minutes may be required. Longer exposure times (i.e., the time that the bacteria are in contact with the product) give better antimicrobial benefits. The importance of time depends both on the pH of the product and on the formula concentration. At high pH (≥ 11.5) and high concentrations, antibacterial efficacy is achieved quickly. At lower pH values (pH ≤ 11) and lower formula concentrations, a longer period of exposure time is required to achieve the same efficacy.

Higher pHs are also better, in general. This factor is important for the product's performance on the Gram negative bacteria, e.g., Escherichia coli and Pseudomonas species. Higher product pH's produce quicker and more complete kill. The opposite is true for the Gram positive bacteria, e.g., Staphylococcus aureus.

Performance is equal to, or slightly better, as the pH is lowered from 11.5 to 9.5. However, this is only true when the formula contains oleic acid.

As stated above, higher formula concentrations (when done independently of pH) enhance the antimicrobial efficacy of the product. The presence of oleic acid is likely a key factor for the performance on Gram positive organisms like S. aureus, while the pH is probably a bigger factor for the Gram negative bacteria, e.g., E. coli and Pseudomonas species.

All parts, percentages, and ratios herein are "by weight" unless otherwise stated. All number values are approximate unless otherwise stated.

Example 1

The following Example illustrates, but is not intended to be limiting thereof, the compositions and processes of this invention wherein the essential foam component is provided through a foaming spray head. The exemplified basic liquid composition can be prepared at pH 9.5-12.5 by dissolving the ingredients in water or water-ethanol using conventional mixing apparatus. In a convenient mode, water is placed in a mixing vessel. Potassium hydroxide, any phosphoric acid, any citric acid, any bicarbonate, glycerine (processing aid), and any ethanol are added in the named sequence, with stirring. The oleic acid is added with high shear and stirring is continued. The PEG (which can conveniently be predispersed in water) is then added. The optional perfume ingredients can be added any time after the oleic acid has been dissolved in the mixture.

A typical toxicologically acceptable cleaning solution composition useful in the methods and articles described herein is as follows:

Ingredient	% Wt.
	Active
Water	89.99
Oleic Acid	2.64
Ethyl Alcohol	2.00
Potassium Hydroxide	2.32
Sodium Bicarbonate	2.00
Citric Acid	0.52
Oil Grapefruit Terpenes	0.03
PEG 3350	0.50

In the test summarized below, identical cleaning compositions were placed in similar spray articles, one with a foaming spray nozzle and the other with a non-foaming spray nozzle. Consumers were then asked to use the product to clean food surfaces, including apples. The results are summarized below:

Test Design: Paired Comparison	Foaming Spray Head	Non-Foaming Spray Head
Food Wash/Rinse Attribute (%):		
- Overall Preference	69	- 31
- Sudsing Preference	67	33
- Feels More Slimy	35	65
- Easier to Rinse	55	45
- Feels Cleaner	62	38
- Removes More Wax From Apples	59	41
Intensity Ratings (Avg.)		
Sudsing (1= none 9=extreme)	6.1	4.0
Sliminess (1= no slim 9=extreme	4.1	4.9
slim)	3.3	3.1
Rinse Ease (1= easy 9=very		
difficult)		

Surprisingly, consumers were shown to prefer the foaming embodiment of identical cleaning compositions by a greater than 2:1 margin. Interestingly, the foaming article was perceived as performing with less "Sliminess" and as only fractionally more difficult to rinse off.

WHAT IS CLAIMED IS:

- 1. An article of manufacture comprising a spray container, suitable for use by an individual to clean produce and edible animal protein, containing a toxicologically acceptable cleaning solution, said cleaning solution being capable of being dispensed with a clearly visible content of foam from said container.
- 2. The article of Claim 1 wherein said article is capable of dispensing a foam that remains visible for at least 3 seconds optionally for at least 1 minute.
- 3. The article of Claim 1 or Claim 2 wherein said spray container further comprises a foaming spray head.
- 4. The article of Claim 3 wherein said foaming spray head is trigger-type.
- 5. The article of Claim 1 wherein said toxicologically acceptable cleaning solution further comprises a non-detergent foam enhancing component, optionally selected from polymeric shear-thinning thickeners, optionally at a level of from about 0.001% to about 1%, or from about 0.005% to about 0.5%.
- 6. The article of Claim 5 wherein said polymeric shear thinning thickeners are selected from the group consisting of substituted celluloses, modified polysaccharides, and naturally occurring gums, optionally from about 0.001% to about 1% of xanthan gum.
- 7. The article of any of Claims 1-6 wherein said toxicologically acceptable cleaning solution comprises all GRAS ingredients.
- 8. An article of manufacture comprising a spray container, suitable for use by an individual to clean produce and edible animal protein, containing a toxicologically acceptable cleaning solution comprising:
 - (a) from about 0.01% to about 15% of C₈-C₁₈ fatty acid;
 - (b) optionally, from about 0.1% to about 4% by weight of nonionic surfactant;
 - (c) optionally, from about 0.1% to about 4% by weight of organic polycarboxylic acid;

- (d) optionally, up to about 0.2% by weight of base-stable anionic surfactant;
- (e) optionally, toxicologically-acceptable basic buffer,
- (f) optionally, toxicologically-acceptable preservative;
- (g) optionally, at least about 0.05%, by weight, of water-soluble polyethylene glycol having a molecular weight of about 200, or higher;
- (h) optionally, from about 0.05% to about 10% of phosphoric acid; and
- the balance comprising an aqueous carrier selected from water and, optionally, low molecular weight, toxicologically-acceptable organic solvent;

wherein said cleaning solution has a pH of from about 9.5 to about 12.5; and said cleaning solution being capable of being dispensed with a clearly visible content of foam from said container.

- 9. A method for cleaning produce and edible animal protein whereby a toxicologically acceptable cleaning solution is dispensed to the surface of said produce and edible animal protein as a visible foam, said toxicologically acceptable cleaning solution optionally having a pH of from about 8 to about 12.5, and/or optionally having all GRAS ingredients.
- 10. The method of Claim 9 comprising the step of contacting the surface of said produce and edible animal protein with said visible foam for a time of at least 3 seconds using the article of manufacture of any of Claims 1-8.

INTERNATIONAL SEARCH REPORT

Inte Ional Application No PCT/US 97/19789

A. CLASSI IPC 6	FICATION OF SUBJECT MATTER A23P1/00 C11D17/04 C11D3/22	C11D9/22		
According to	o International Patent Classification (IPC) or to both national classification	tion and IPC		
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IPC 6	ocumentation searched (classification system followed by classification A23P C11D	n symbols)		
Documenta	tion searched other than minimum documentation to the extent that su	ch documents are included in the fields sea	rched	
Electronic d	ata base consulted during the international search (name of data bas	e and, where practical, search terms used)		
C. DOCUM	ENTS CONSIDERED TO BE RELEVANT			
Category '	Citation of document, with indication, where appropriate, of the rele	vant passages	Relevant to claim No.	
X	WO 95 12326 A (PROCTER & GAMBLE) 1995	11 May	1,3,4, 7-9	
Y	see page 14, line 8 - line 14; cl example III	aims;	1-10	
Y	WO 91 14759 A (PROCTER & GAMBLE) 1991	3 October	1-10	
	see page 7, line 21 - line 25; cl	aims 1,8		
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Fut!	her documents are listed in the continuation of box C.	X Patent family members are listed in	annex.	
* Special ca	tegories of cited documents :	T" later document published after the inter		
"A" document defining the general state of the art which is not crited to understand the principle or theory underlying the considered to be of particular relevance				
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citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or document is combined with one or more other such docu-				
"P" docume	means ent published prior to the international filling date but nan the priority date claimed	ments, such combination being obviou in the art. "&" document member of the same patent f		
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	Fax: (+31-70) 340-3016	Loiselet-Taisne,	S	

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inte Ional Application No PCT/US 97/19789

Patent document cited in search report	Publication date	Patent tamily member(s)	Publication date
WO 9512326 A	11-05-95	US 5549758 A	27-08-96
		US 5500143 A	19-03-96
		US 5500048 A	19-03-96
		US 5498295 A	12-03-96
		US 5503764 A	02-04-96
		AU 1043695 A	23-05-95
		BR 9407963 A	03-12-96
		CN 1139373 A	01-01-97
		EP 0726717 A	21-08-96
		JP 9505996 T	17-06-97
		US 5705461 A	06-01-98
		ZA 9408585 A	26-06-95
WO 9114759 A	03-10-91	AU 7457191 A	21-10-91
	00 10 01	CA 2078443 A	28-09-91
•		CN 1064013 A	02-09-92
		EP 0521893 A	13-01-93
		NZ 237582 A	27-09-94